# Speciated PMcoarse by Difference:

## A look at a year of XRF data in New York City and in Niagara Falls, New York

National Monitoring Conference Las Vegas, Nevada November 6 - 9, 2006

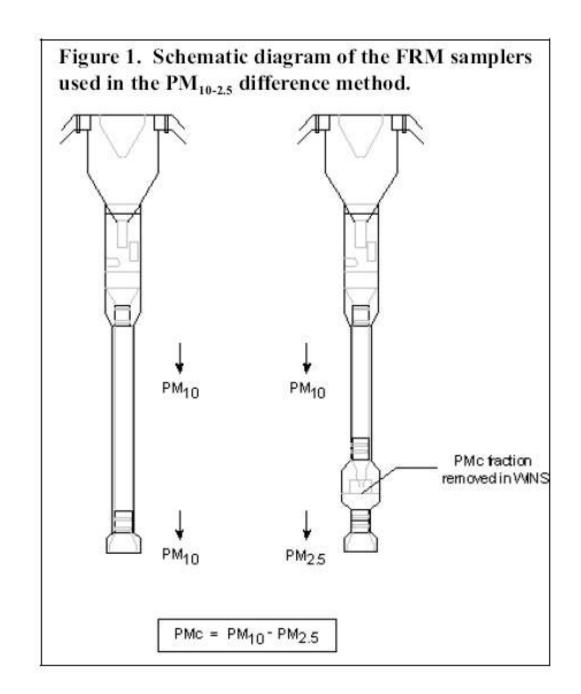
Dirk Felton, Kevin Civerolo and Oliver Rattigan

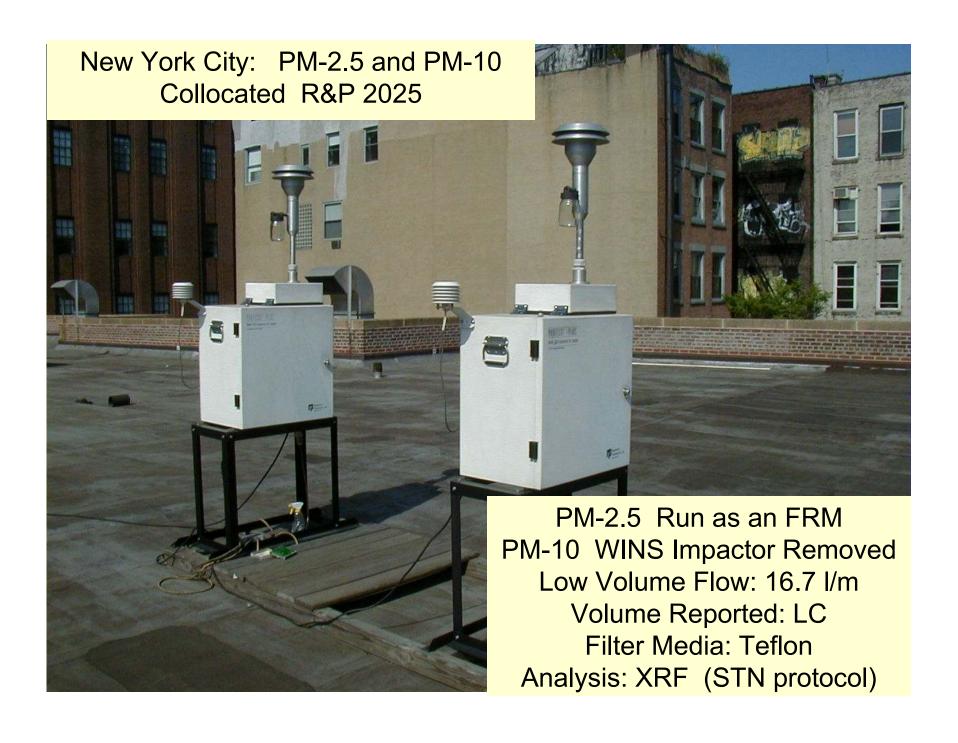


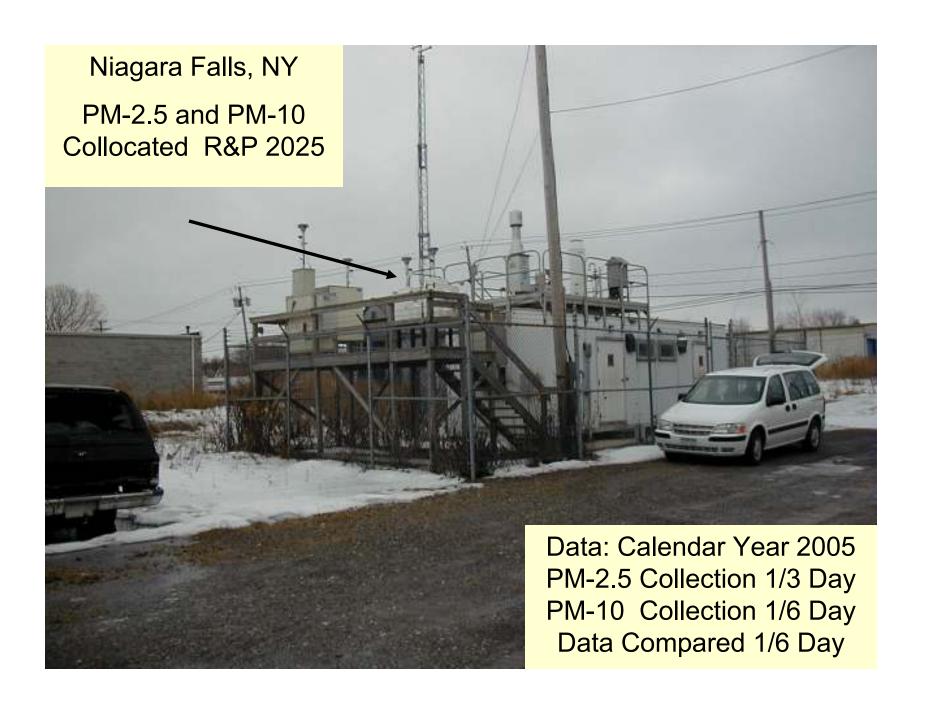
The FRM for PMc utilizes two PM-2.5 FRMs

The WINs impactor is removed in the PM-10 sampler. A bypass tube is installed in the inlet in place of the impactor.

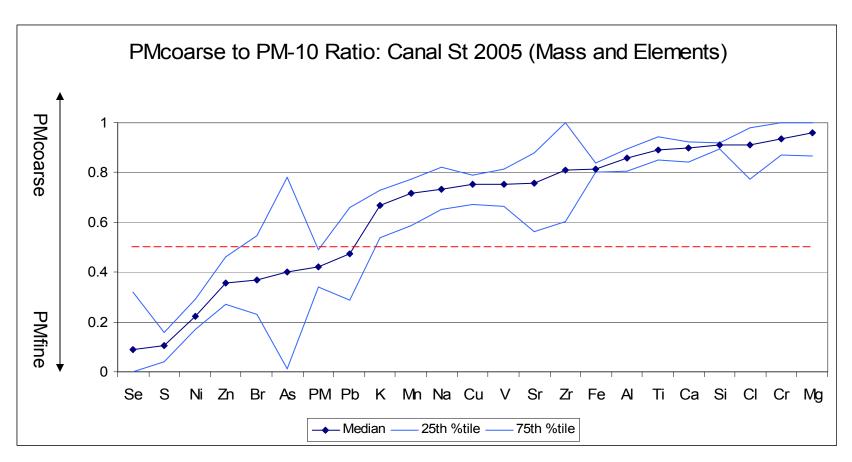
All other aspects of the PM-2.5 FRM sample collection protocol are followed for both filters



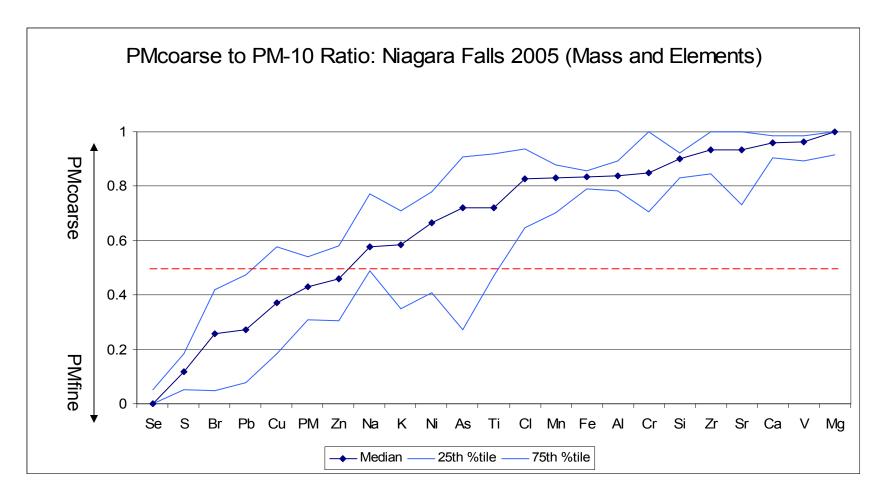




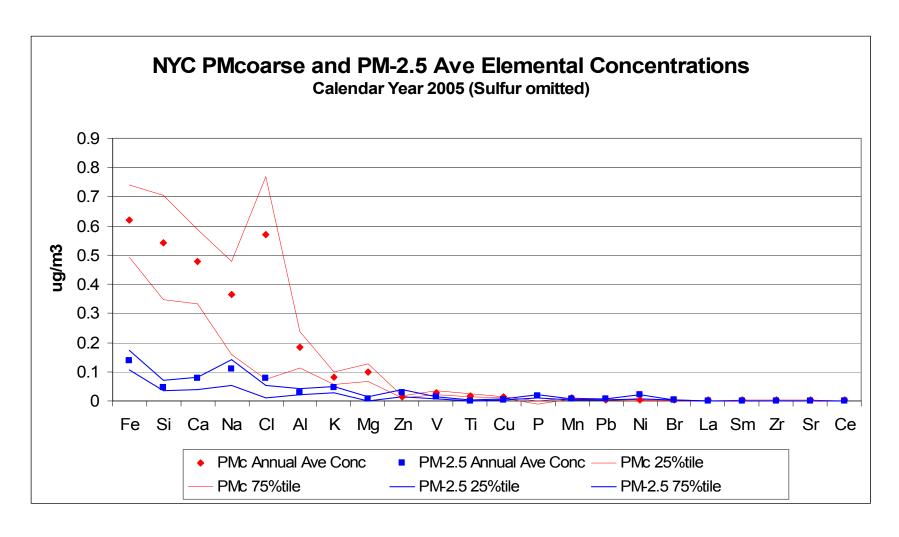
Ratios are useful for determining the predominant size fractions Elements above .5 are found predominantly in the Coarse mode Elements below .5 are found predominantly in the Fine mode The ratio for PM is about .4 so most of the mass is in the fine mode



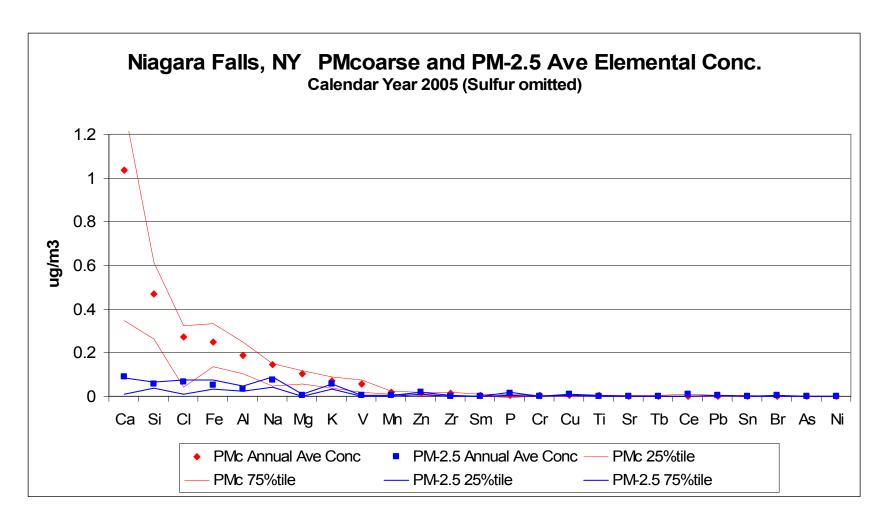
Some elements are consistently found in either the Fine or the Coarse mode S is always in the fine mode Ca and Mg are nearly always in the Coarse mode The order of elements (X-axis) varies by location The 25<sup>th</sup> and 75<sup>th</sup> percentiles indicate the consistency of the size mode



# PMcoarse concentrations for 8 to 10 elements are much larger and more variable then PM-2.5 elemental concentrations Sulfur is omitted due to the scale but it is 99% in the fine mode

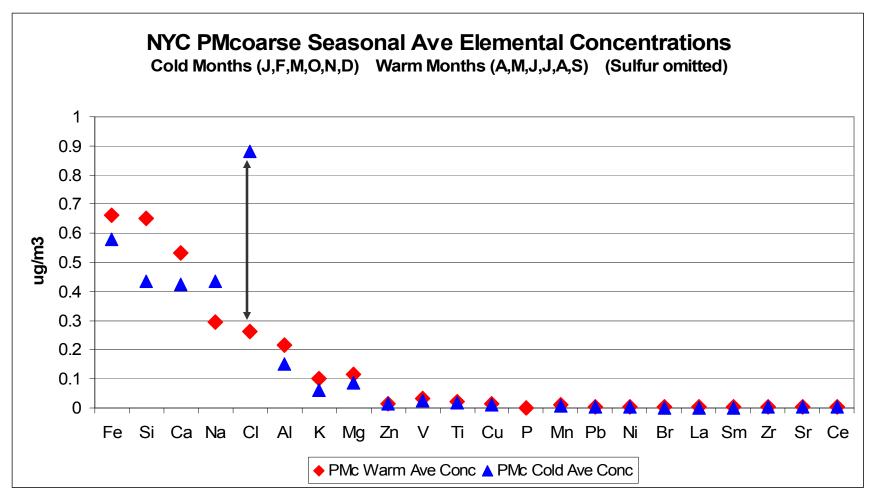


The crustal components Ca, Si, Fe, Al are the predominant coarse species at this site which is adjacent to an unpaved road The PM-2.5 data do not indicate a strong crustal impact

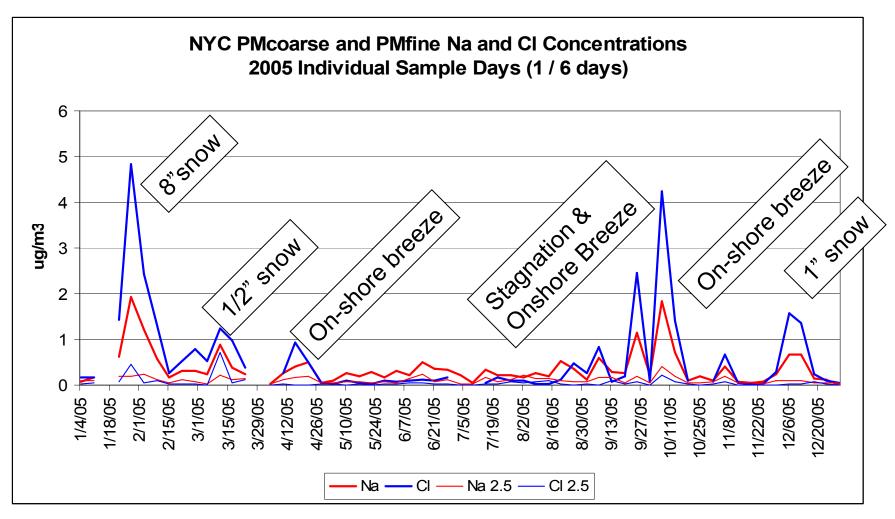


The high CI and Na concentrations in the cold months indicates a significant chlorine source in addition to a road salt source The highest CI concentrations occur over 7 days in 2005

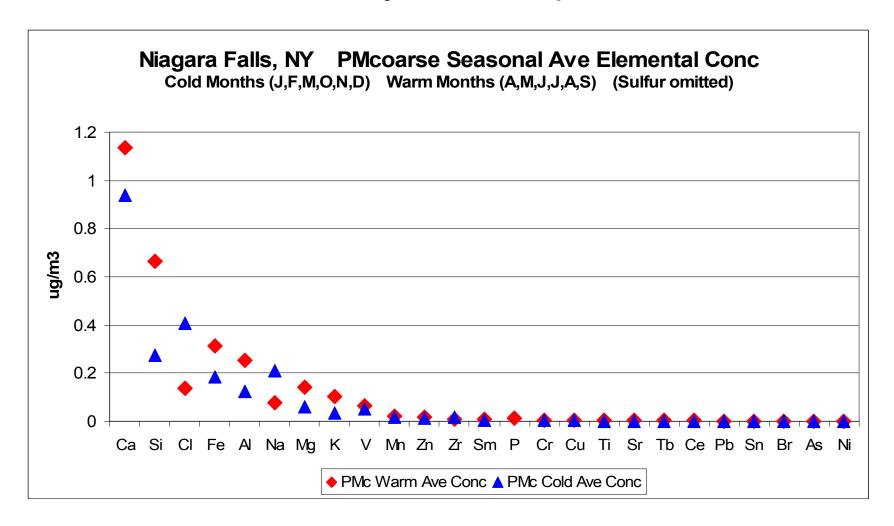
The crustal components (Ca,Si,Fe,AI) are higher in the warm months



The 7 days when CI and Na concentrations were high were coincident with snowfall, on-shore ocean breezes and stagnation events The CI and Na PM-2.5 concentrations show much less of a response to these sources



Na and CI are higher in the cold months but not as much as in NYC
The higher cold ratio of Na to CI is consistent with road salt composition
The crustal species (Ca,Si,Fe,AI) are significantly higher in the warm
months. This site is adjacent to an unpaved road



#### Caveats:

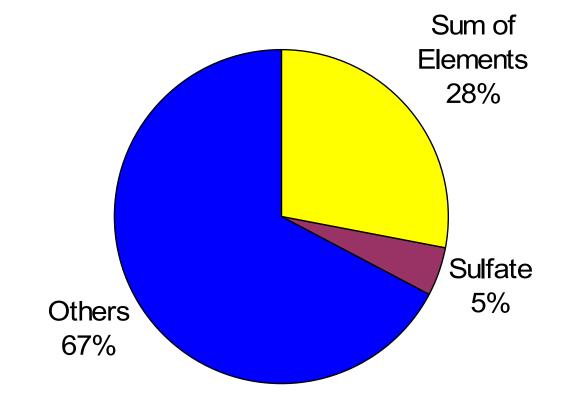
PMcoarse Speciation by difference is not useful for elements that are predominantly found in the fine mode

When a large PM-2.5 concentration is subtracted from a slightly larger PM-10 concentration; the resulting difference is small in relation to the additive error from each measurement

The error can be reduced by looking at averages of many measurements rather than individual sample days

# Elemental Speciation of PMcoarse Mass in NYC accounts for approximately one third of the PMcoarse Mass

Mass determination and XRF analysis probably will not provide enough information for source attribution analysis or health effects studies



# The EPA evaluated candidate continuous PMc instruments against PMc by difference in Gary, IN, Phoenix, AZ and Riverside, CA in 2003 and 2004

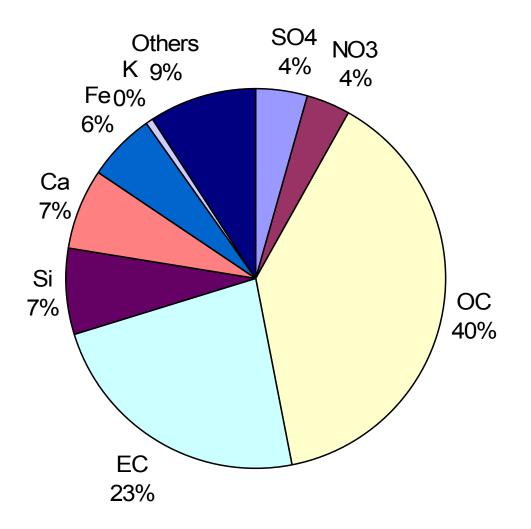
Pairs of PM-2.5 and PM-10 FRMs were operated with Teflon filters for Mass, Sulfate and Nitrate and with Quartz filters for OC and EC

The speciation data were collected to help explain the differences between the candidate continuous PMcoarse instruments



Speciation data for the field tests was provided by EPA's Office of Research and Development in RTP, NC

### Gary, Indiana PMcoarse Species Data Data Collection: Mar 6 – April 6, 2003 PMc = 27.3 ug/m<sup>3</sup>



### **Species Mass Adjustments**

SO4 is all amm. sulfate = 1.375\*SO4

NO3 is all amm. nitrate = 1.29\*NO3

OC converts to organic mass with 1.8 multiplier

EC = EC

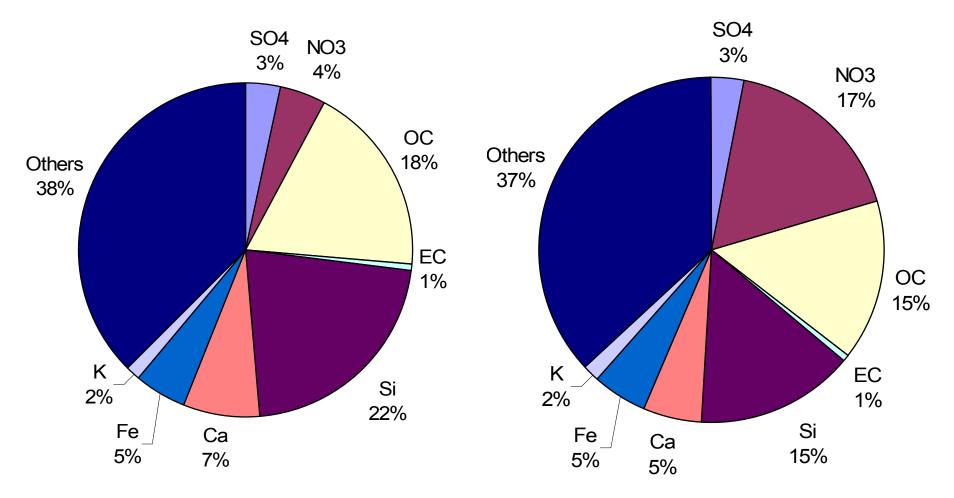
Si is all SiO2 = 2.14\*Si

Ca is all CaO = 1.40\*Ca

K is all K2O = 1.2\*K

Fe is all Fe2O3 = 1.43\*Fe

### In both Phoenix and Riverside, the "Others" category is significant



Phoenix, AZ
Data: May 14 – June 14, 2003
PMcoarse = 35.2 ug/m<sup>3</sup>

Riverside, CA
Data: July 23 - Aug 23, 2003
PMcoarse = 33.3 ug/m<sup>3</sup>

#### **Conclusions:**

Only 10 of the 48 elements analyzed by XRF are found in high enough concentrations in the coarse mode in NY to provide useful PMcoarse by difference

### PMcoarse by difference can:

Determine the site specific impact of crustal materials from sources such as unpaved roads and agricultural tilling

Determine and differentiate the impact of crustal salts from sources such as road salting and sea salt

Source attribution models that are limited to PMcoarse elements are not likely to be effective for sources other than crustal materials and salts particularly in sites representative of large scales. These models may be effective close to a source with unique PMcoarse elemental emissions

#### **Conclusions Continued:**

The high proportion of un-identified mass in Phoenix and Riverside demonstrates that our current understanding of the composition of coarse particles is insufficient

#### Research is needed to:

Determine if analysis techniques and mass adjustment factors are geographically appropriate and appropriate for the particles in the PMcoarse size fraction

Obtain a geographically and seasonally representative understanding of coarse particle composition before a National PMcoarse speciation program is implemented